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Report No. 9

Scientific Report No. III

THE EFFECT OF CONCENTRATED LIGHT ON PHOTOCHEMICAL ENERGY CONVERSION BY NITROSYL CHLORIDE SOLUTIONS

Prepared for:

GEOPHYSICS RESEARCH DIRECTORATE
AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS

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ABSTRACT

Experiments on the photolysis of nitrosyl chloride in carbon tetrachloride solution with unconcentrated sunlight are reported. These experiments showed that quantum yields and amount of energy stored with unconcentrated light were only 1/10 of quantum yields and amount of energy stored with concentrated light. With this finding one of the aims of the present research program has been achieved by showing that concentrated light considerably increases the output of a photochemical reaction.

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I INTRODUCTION

The present research project extends the research done under Contract No. AF 19(604)-3477, in which the solar furnace was used for the first time as a cool, intense light source. During the former project, two energy-storing reactions were studied at the focus of a solar furnace. Of these two reactions the cerous-ceric system produced greatly increased quantities of oxygen over those produced by unconcentrated sunlight, but did not produce measurable quantities of hydrogen; hence the possibility of using the system for solar energy storage in the earth's atmosphere was remote. Initial experiments with a closed nitrosyl chloride-carbon tetrachloride system showed that only a small amount of nitrosyl chloride was decomposed--that is, the photostationary state was far on the reactant side. The reason for the small net amount of decomposition was the fast rate of recombination of the photoproducts.

The present project consists of experimental investigations directed toward:

1. Design, construction, testing, and operation of various flow systems for the photolysis of nitrosyl chloride as an energy-storing reaction. The purpose of the flow system is to remove the evolved gases from the system before they can recombine to form nitrosyl chloride.

2. Study of other promising systems for conversion and storage of solar energy. If such promising systems are found, their efficiency for energy conversion and storage will be determined.

II PAPERS PUBLISHED UNDER THIS AND PREVIOUS (AF 19(604)-3477) CONTRACTS

1. Photochemistry in the solar furnace. Ind. Eng. Chem. 51, 1335 (1959)

2. Photochemistry in the solar furnace--parallel light and spectral distribution. Ind. Eng. Chem. 52, 377 (1960)

3. A new solar furnace--design and operation. Ind. Eng. Chem. 52, 825 (1960)

4. Photolysis of nitrosyl chloride in the solar furnace. Solar Energy 4 (2), 1 (1960)

5. Photochemical systems for solar energy conversion--nitrosyl chloride. Solar Energy 5, 44 (1961)

6. Chemical conversion and storage of concentrated solar energy. Agenda Item II D 2, United Nations Conference on New Sources of Energy, Rome, Italy, August 1961

7. Flow systems in the solar furnace and the photolysis of nitrosyl chloride. Solar Energy 5, 121 (1961)

III SUMMARY AND CONCLUSIONS

In Scientific Report No. II we reported the design, construction, installation, testing, and use of various flow systems in a two-foot-diameter solar furnace. These flow systems were used to determine the amount of energy stored by photolysis of nitrosyl chloride in carbon tetrachloride solution. Since the amount of energy stored by use of this apparatus was ten times larger than it was without use of the flow system and approached that of natural systems such as green plants, we wished to determine whether this increase was due to an efficient flow system or to the use of concentrated light.

Experiments in which the same efficient flow system is used with unconcentrated light are described in this report. By comparing results of those experiments with results obtained by use of concentrated light, we conclude that use of concentrated light resulted in the significantly higher yields described above.

IV PHOTOCHEMICAL EXPERIMENTS WITH CONCENTRATED LIGHT SOURCES

The ultimate quantum yield of a simple photochemical reaction is unity.[1] Few such reactions exist; quantum yields near unity can be obtained for some other reactions under ideal conditions, but many factors tend to reduce the measured quantum yield. Among these factors are polychromatic light, large reaction mass or volume, light saturation, and back reactions. These same factors also affect the efficiency of photochemical energy conversion reactions.

The rate (R) of photochemical reactions usually is proportional to the light intensity (I):

$$R = kIc \qquad (1)$$

where k is the rate constant extrapolated to zero light intensity and c is the active concentration(s) of the reactant(s). An increase in light intensity would, therefore, increase the reaction rate linearly. We have reported a series of experiments which have shown that it is possible to gain a greater output, although not necessarily greater efficiency, from photochemical reactions by concentrating light on the vessel in which the reaction occurs. For instance, we increased the rate of production of oxygen in the photoreduction of ceric perchlorate

$$H_2O + 2Ce^{+4} \xrightarrow{h\nu} 2Ce^{+3} + 2H^+ + 1/2\ O_2 \qquad (2)$$

by a factor of 10^6 by using concentrated sunlight in a solar furnace rather than unconcentrated sunlight.[2,3]

We have also examined the rate of production of nitric oxide in the photolysis of nitrosyl chloride in carbon tetrachloride solution with concentrated sunlight:[4,5,6]

$$2NOCl(sol) \xrightarrow[CCl_4]{h\nu} 2NO(g) + Cl_2(sol) \qquad (3)$$

The quantum yield and energy storage for this reaction were found to be 0.22 and 1.71% with concentrated light. The quantum yields are lower than those obtained by others[7,8] as would be expected for this higher light intensity. The energy storage obtained with concentrated light (as a percentage of total incident sunlight) cannot be compared directly with that obtained by other authors. However, it is about one-half of the energy storage obtained with an optimum mass culture of algae[9] and is of the same order of magnitude as other photosynthetic converters.[10] Since the photolysis of nitrosyl chloride is a completely inorganic reversible reaction, this amount of energy storage encourages further search for other, yet more efficient photochemical energy conversion reactions.

One factor in the foregoing experiment which needed further checking was the question of whether the quantum yield and energy storage had been increased by the use of concentrated light, or whether they might have been increased by use of the new and perhaps more efficient flow system which was designed for use with unconcentrated sunlight. This experiment will be described in this report.

V EXPERIMENTAL DATA

An insolation cell for the absorption of unconcentrated sunlight was constructed by sealing a polished vycor plate to a rectangular pyrex vessel. The dimensions of the insolation cell were 8-1/4 x 8-1/4 x 1-3/4 inches. The cell was mounted on the Springfield equatorial mount described previously[3] for use with our solar furnace. In operation the vycor plate was always normal to the incoming sunlight; furthermore, the spectral distribution of the incoming sunlight was not appreciably altered by passage through the vycor plate.[3]

This insolation cell was connected to a flow system identical with system 7 of reference (6). The complete system is shown in Fig. 1. It consists of a Teflon pump with a Kel-F elastomer liner,* connected to a 1/4-hp General Electric Company Half-Wave Thymotrol drive, direct-current motor, a surge vessel, a solution storage vessel, and a gas storage vessel. Three mercury manometers were used to measure pressure in the surge tank, the solution storage vessel, and the gas storage vessel.

The system was filled with solutions of nitrosyl chloride in carbon tetrachloride and the insolation cell was darkened with aluminum foil. After the pressure had steadied in the three parts of the system, the cover was removed, thus exposing the insolation cell to sunlight. A number of such light and dark cycles were observed.

It was noted before[6] that the salient variable in this flow system is not the pressure in each part of the system, but rather the sum of the pressure-volume products (ΣPV) of each part of the system. This variable remains steady in the dark, rises upon exposure to light, and falls again in the dark. A typical run, expressed in this variable, is shown in Fig. 2. It compares well with rate curves obtained in previous work with concentrated light.

*Model XB-T6, maximum capacity 1 gpm H_2O at 70°F, 0 psig. Vanton Pump and Equipment Corp., Hillside, N. J.

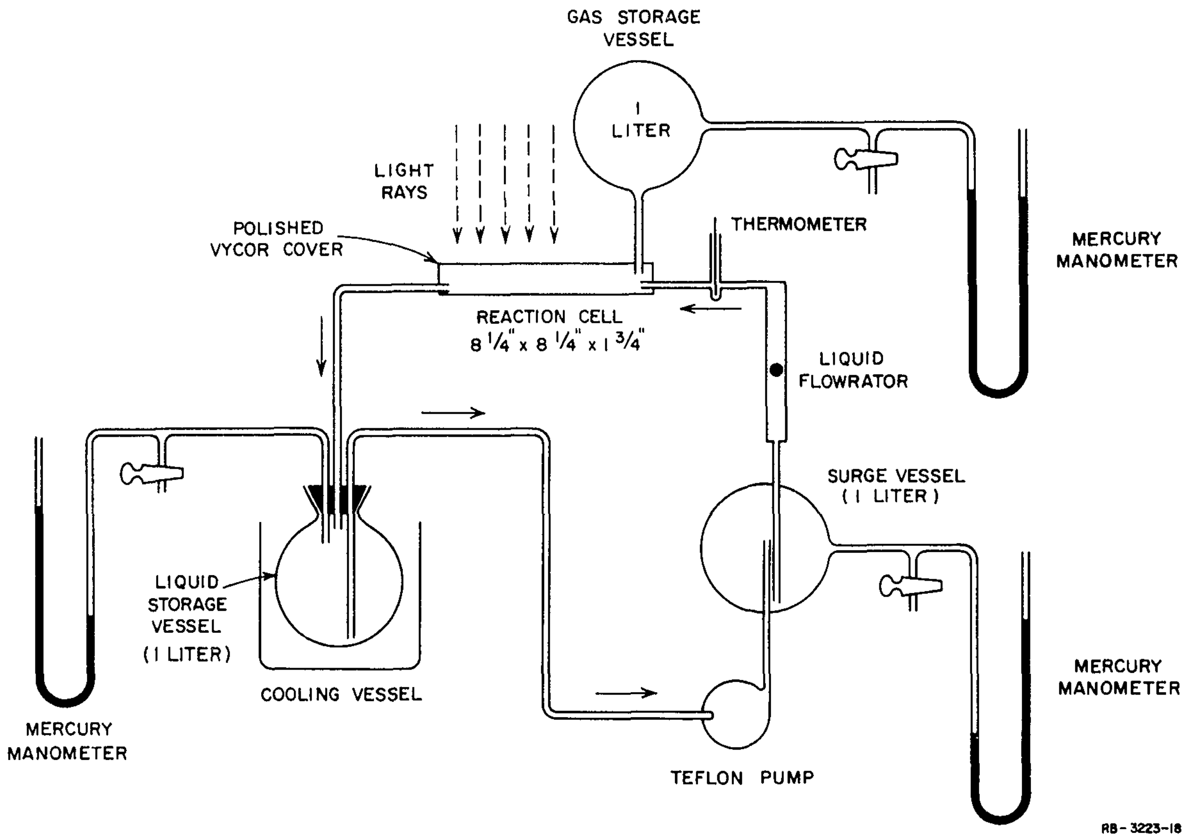

FIG. 1 FLOW SYSTEM FOR LIQUID PHASE PHOTOCHEMICAL REACTIONS WITH UNCONCENTRATED LIGHT

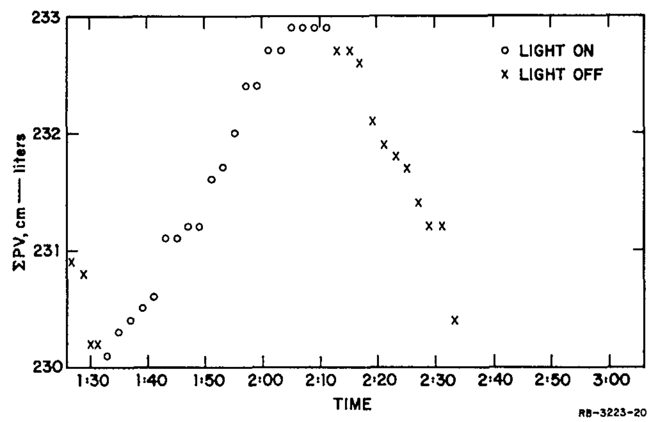

FIG. 2 RESULTS OF TYPICAL EXPERIMENT WITH UNCONCENTRATED LIGHT

VI DISCUSSION OF RESULTS

The results obtained here with unconcentrated sunlight, by analogy to those obtained with concentrated sunlight,[6] may be expressed in terms of the photodissociation of nitrosyl chloride and of the recombination of the photoproducts, nitric oxide and chlorine. The pressure rise upon exposure to light (Fig. 2) rapidly approaches a steady state. The location of the steady state is governed by the speed of the back reaction.

Once the steady state has been established, the gas is generated only as fast as it is consumed by the back reaction. On the other hand, if the gas were withdrawn continuously to feed a nitrosyl chloride fuel cell, the steady state would be upset and the gas would be generated at the rate at which it is generated in the approach to the steady state in our experiments.

The net rate (R_n) of reaction (3), which is the quantity we observe, is the difference between the forward rate (R_f) and the backward rate (R_b). The latter can be calculated from known rate constants

$$R_n = R_f - R_b = k_f I(NOCl) - k_b (NO)^2 (Cl_2) \qquad (4)$$

These calculations are carried out for duplicate runs in Table I. It should be noted that the backward rate is only one percent of the net rate, and that the rate of gas evolution perforce decreases to that value when the steady state is established.

Nitrosyl chloride in solution absorbs light fairly continuously[5,11] between 3000 Å and 6300 Å. This absorption covers 38% of the solar spectrum.[6] The surface area of the insolation vessel is 440 cm^2, so the rate of energy collection is 334 cal/min in the 3000-6300 Å wavelength range. Taking the average energy of a mole of photons (one einstein) as 64 kcal/einstein in that wavelength range, we have 5.22×10^{-3} einstein/min

Table I

RATES, QUANTUM YIELDS, AND CALCULATED ENERGY STORAGE FOR PHOTOLYSIS OF NITROSYL CHLORIDE IN UNCONCENTRATED SUNLIGHT

		Experiment 36	Experiment 39
Net rate of gas evolution	moles/liter-min	2.9×10^{-5}	2.4×10^{-5}
Rate of backward reaction $2\ NO + Cl_2 \longrightarrow 2\ NOCl$	moles/liter-min	2.4×10^{-7}	1.8×10^{-7}
Rate of forward reaction $2\ NOCl \longrightarrow 2\ NO + Cl_2$	moles/liter-min	2.9×10^{-5}	2.4×10^{-5}
Net quantum yield		0.018	0.015
Quantum yield for forward reaction		0.018	0.015
Initial NOCl concentration	moles/liter	0.141	0.062
Flow rate	liter/min	1.065	1.065
Light saturation factor	%	4.3	7.9
Maximum energy storage	cal/min	0.46	0.38
Energy storage in 3000-6300 Å wavelength range	%	0.14	0.11

intercepted by the surface of the insolation vessel. This figure enables us to calculate a quantum yield, which is listed in Table I. As in previous experiments, these rough quantum yields have been obtained without knowing optimum values of such experimental parameters as concentration, flow rate, and configuration of insolation cell, and also without extrapolation to zero light intensity. They are to be compared with the quantum yields obtained in experiments with concentrated light, and were determined under comparable conditions.

The other quantities listed in Table I are added for comparison with the concentrated light system. The light saturation factor compares the number of molecules of nitrosyl chloride in the vessel with the number of photons incident on the vessel in unit time. The rate of energy storage is the product of photon flux (5.22×10^{-3} einstein/min), quantum yield, and free energy of recombination of nitric oxide and chlorine (4.9 kcal/mole). The efficiency of this storage is computed by dividing the rate of energy storage by the rate of energy collection (334 cal/min).

We have previously compared[6] quantum yield and energy storage of the photolysis of nitrosyl chloride with concentrated light in both flow and static systems. Both the quantum yield and the energy storage were ten times higher in the flow system than in the static system; this increase was attributed to better separation of the photoproducts in the flow system. We can now compare quantum yield and energy storage in a flow system with both concentrated and unconcentrated light (Table II). Both the quantum yield and the energy storage are 14 times higher in concentrated light than in unconcentrated light.

Table II

SUMMARY OF EXPERIMENTAL RESULTS

	Average Quantum Yield	Average Energy Stored as Percentage of Available Energy in 3000-6300 Å Range
Concentrated light		
Flow system	0.22	1.71
Static system	0.023	0.18
Unconcentrated light		
Flow system	0.016	0.12

While the introduction of the flow system has reduced the back reaction rate sufficiently to make meaningful observations possible, the experiments reported here show that the increased energy storage of nitrosyl chloride in the solar furnace is due to the concentrated light, as would be expected from Equation (1).

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